Answer to Interactive comment By Stefan Persijn, VSL (Dutch Metrology Institute), spersijn@vsl.nl, Received and published: 16 April 2019
on
Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2019-130, 2019, entitled: "Caution with Spectroscopic NO_2 Reference Cells (Cuvettes)" by Ulrich Platt and Jonas Kuhn.

Answer:
We like to thank Stefan Persijn for his interesting and constructive comments, which we answer in the following. The comments are reproduced in slant font followed by our answers in normal font.

Interesting paper on the reactions occurring in NO2 reference cells used in e.g. DOAS spectrometers.
A few remarks:

1) Any comparison with experimental observations (either from the authors own experiments or from literature) is missing. It is suggested to add such a comparison (if these data are available).

Answer: This is a theoretical study, meaningful experimental data from cuvettes do not appear to be available in the literature. Special measurements to 'validate' NO_X reaction system, which extremely well studied in the laboratory (see reaction kinetic data compilation JPL 15-10, Burkholder et al. 2015 as referenced in our manuscript) appear to be a waste of time.

2) NO2 cannot be obtained at high purity from commercial gas suppliers. Some comment could be added about this (i.e., starting mixture will already be more complex).

We like to thank you for this comment. Although neither the basis for this statement nor any quantitative information is given, it appears to be plausible and we shall add a comment in the revised version of the manuscript saying that 'In fact, when buying NO_2 from a manufacturer some of the described reactions can already proceed in the initial gas, which therefore might already contain impurities (e.g. of NO, HONO and HNO_3)'.

3) Page 11 "One can actually assume that all H2O is ultimately converted to HNO3, sequestering equivalent amounts of NO2 and water. " This might be expected but apparently this does not happen. At VSL we did some experiments adding water to NO2 mixtures and only a relatively small part of the water is eventually converted to HNO3. (see https://www.hindawi.com/journals/jspec/2018/9845608/).

Answer: In the quoted publication (S. Persijn, Purity Analysis of Gases Used in the Preparation of Reference Gas Standards Using a Versatile OPO-Based CRDS Spectrometer, J. of Spectroscopy, Vol. 2018, Article ID 9845608) some experiments

are described, where 2 ppm water (vapour) were added, leading to the formation of gas phase HNO_3 amounting to between 2 and 25% of the added water. Since it is likely that a good fraction of HNO_3 formed will stay at the walls of the vessel (this problem is also pointed out in the publication), these figures have to be regarded as lower limits of the H_2O to HNO_3 conversion. Moreover, the experiments were performed at very low (for absorption cells) NO_2 mixing ratios of only 10 ppm, thus N_2O_4 formation should be negligible. Also the time between water addition and HNO_3 measurement is not given. Therefore we can not see the evidence for the statement that H_2O may not be quantitatively converted to HNO_3 in an environment containing very high (e.g. thousands of ppm's) NO_X levels.
In fact our model calculations (see Figures 4 to 8 of the revised version) that water is quickly lost in the cell.

4) Topping with dry synthetic air is probably preferred over filling with laboratory air (p11).

Answer: We actually write in section 5.2 that we recommend topping with dry air or oxygen. Whether synthetic air is sufficiently dry is a good question. We would prefer air (or better oxygen as pointed out e.g. in the Examples on page 7 and section 5.2), which is dried by a cartridge with drying agent (e.g. molecular sieve) in a cartridge.

5) In equation R20 on page 11 the value of the rate constant is missing.

Answer: Thank you for pointing out this omission, which we will correct in the revised version. Note, however, that the value of k_{20} (and its temperature dependence) is given in Table 1 of our manuscript.

6) The section on the path length of the optical cells (section 2) is not relevant for the rest of the paper and should be omitted here.

Answer: We disagree with this statement. Our manuscript is about potential problems with NO_2-cells not only about chemistry in cuvettes. We therefore, find it natural and necessary to also report on other effects influencing the apparent optical density of a cuvette.